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Epitaxial thin NiO films grown on Fe(001) and the effect of temperature

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Abstract

Thin NiO(001) films have been epitaxially grown on a ferromagnetic Fe substrate. They have been investigated by X-ray photoemission and spin-resolved inverse photoemission spectroscopies, and compared with films grown in the same conditions on Ag(001). Well ordered and good quality films are obtained in most cases, while defect states within the fundamental gap are detected only in few cases. Upon annealing these films above 600 K a Ni–Fe substitution reaction occurs in the film, leading to the formation of an Fe oxide film at the surface, while Ni atoms dissolve into the substrate.

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1. Introduction

Oxide thin films and metal–oxide interfaces play a fundamental role in many chemical–physics processes and applications in material science [1], and are involved in various important technological areas ranging from catalysis [2] to magnetism [3]. More recently, oxide thin films on metal substrates have also been used as model systems for the investigation of the properties of bulk oxides and their surfaces. In particular high quality films can be prepared in ultra high vacuum (UHV)

condition by epitaxial growth on well characterized and clean single crystal surfaces [4]. Single crystalline oxide barriers between ferromagnetic (FM) metal layers constitute ideal systems for the preparation of tunneling magnetoresistance junctions [5,6], which are important for the development of magnetic random access memory devices [7]. Moreover, if the oxide is antiferromagnetic (AFM), as it is the case in many transition metal oxides, a rich phenomenology at the FM–AFM interface occurs [8], related to the exchange bias mechanism, with several possible technological applications [9].

From a fundamental point of view, solid oxides constitute a benchmark for electronic structure theories, due the strong electron correlation effects occurring in these materials. In this frame, NiO thin films acquire a particular relevance. In

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fact, this material was considered long ago as a prototype system to define the problems that arise in band concept if large electron–electron correlations are present [10]. Since then, a large amount of work on the electronic [11,12] and magnetic [12–14] properties of NiO has been done. Recently very well characterized NiO monocrystalline thin films have been grown by evaporation of Ni in an O₂ atmosphere onto non-reactive metal substrates [15]. We have for example used this method to investigate the empty electronic structure of NiO by measuring inverse photoemission (IPE) spectra from NiO(001) thin films epitaxially grown onto Ag(100) [16]. Besides the very high quality of the grown sample, the thin film structure prevents any problem of charging, even for IPE spectroscopy, and we were able to give a firm experimental basis to the long debated subject of NiO empty states [16].

The key ingredient for a good epitaxial growth is the use of a substrate with a lattice parameter matching closely that of the overlayer: Ag and Au substrates have been successfully used for the growth of NiO [15]. On the contrary, it is known that due to the strong lattice misfit (about 19%) between pure Ni and NiO, thin NiO films do not grow properly onto Ni substrates [17]. Because of the interest in AFM–FM interfaces outlined above, we looked for other FM suitable substrates. As a matter of fact, the Fe(001) surface presents a square-net template very similar to those of Ag(001) and Au(001), and it is indeed well known that Fe(001) films grow epitaxially on both Au(001) and Ag(001), [18–20] and viceversa [18, 19]. By allowing for a 45° rotation of the overlayer lattice with respect to the substrate, as in the Fe–Au and Fe–Ag systems, one gets a misfit of only ~3% between the NiO(001) and Fe(001) surface unit meshes. Thus we have performed the growth of NiO thin films on Fe(001) in the same experimental conditions as those used for the NiO/Ag(001) case. NiO/Fe is a prototype system to study the magnetic behavior of a FM–AFM interface. It has recently been investigated by X-ray magnetic circular dichroism [21] and a decrease of the Fe magnetic moment at the interface with NiO has been reported. A study by spin polarized secondary emission spectroscopy [22] revealed a

nearly perpendicular coupling between the Fe and the NiO lattice spins at the interface. A study on the related Co/NiO system [23] focussed on the dependence of the magnetic properties on the crystal quality of the films. More recently, an X-ray absorption spectroscopy study [24] pointed out that both NiO and CoO are strongly reduced by the deposition of an iron film, in turn oxidized by the presence of the adjacent oxide. The formation of an oxidized Fe interfacial layer has also been observed for deposition of MgO films on Fe(001) [25]. The complex interface resulting from oxide reduction and metal oxidation is expected to play a significant role in the electronic and magnetic coupling between Fe and oxides.

In this paper we present the results of this study: the films have been grown in UHV and investigated in situ by means of IPE (also with spin resolution) and X-ray photoemission spectroscopy (XPS). Our results show that high quality NiO/Fe(001) films can be grown. Furthermore, despite the presence of a magnetized FM substrate, no polarization effect takes place in the spin resolved IPE profiles indicating that the AFM character of the oxide is not broken by the reduced dimensionality of the thin film. Defects formation occurs in few cases in the NiO film and it is seen that their nature preserves charge neutrality. Upon interface annealing complete Fe–Ni exchange takes place in the oxide layer with formation of a crystalline FeO(001) structure.

2. Experimental

The experiments herein reported refer to XPS ($h\nu = 1253.6$ eV, with full width at half maximum FWHM = 1.2 eV) and IPE ($h\nu = 9.4$ eV, FWHM = 0.7 eV) performed in an UHV system (base pressure $< 7 \times 10^{-11}$ mbar) equipped with standard surface characterization techniques [20]. The Fe substrate was prepared by deposition of a thick Fe film on a sputter-cleaned and annealed MgO(001) substrate. As already reported [26], upon annealing relatively thick films (500–1000 Å) at 600 °C, nice Fe(001) single-crystal films are obtained. They show clean and well ordered (001)

surfaces, as revealed by XPS and low energy electron diffraction (LEED), respectively.

NiO(100) is successively grown at room temperature by deposition of pure Ni in oxygen atmosphere. Ni is evaporated by electron beam heating of a Ni rod at a rate of about 0.8 monolayer (ML) per minute, as evaluated by a calibrated quartz microbalance. During evaporation the UHV chamber pressure is kept at 8×10^{-7} mbar by introducing high purity O₂ through an UHV leak-valve. At variance with the case of the Ag(001) surface, however, the Fe substrate cannot be considered as non-reactive. This implies that substrate–oxygen interaction cannot be neglected, so that the initial growth conditions would strongly depend, in an uncontrollable way, on the details of the timing for the O₂ leak-valve opening. In order to avoid such problems we decided to use as starting substrate an oxidized Fe surface, stable with respect to further oxidation. In particular we have chosen the well characterized and stable Fe(001)-p(1 × 1)O surface, obtained by annealing the clean Fe(001) surface exposed to O₂ [27]. With its very sharp (1 × 1) LEED pattern in registry with the Fe substrate and strong spin dependent effects [27,28], this surface is indeed well suited for our purposes. We note also that, even in unintentionally oxidized surfaces, an Fe–O layer is very likely to form at the Fe/metal-oxide interface, as it has been recently reported for the MgO/Fe(001) case [6]. Details on the substrate termination may well influence the properties of ultrathin films and buried interfaces, which are however not addressed here. The present results deals with films having large enough thickness as to mask any contribution to the IPE spectra coming from the substrate and the interface. Different NiO film thicknesses have been prepared in the 10–25 ML range, obtaining very similar results in all cases. For the sake of simplicity, in the following we will refer to these films grown on Fe(001)-p(1 × 1)O substrates as to NiO/Fe(001) films.

3. Results and discussion

High quality NiO films can be grown onto Ag(001) surfaces, as confirmed by numerous

studies, which have allowed to define various spectroscopic criteria for the formation of NiO [12–16]. As noted above, replacing Ag with Fe increases the overlayer–substrate lattice mismatch only very slightly, and as a result we were able to prepare well ordered epitaxial NiO/Fe(001) films. The correct stoichiometry was confirmed by valence band and core level XPS analysis. The films showed a LEED pattern similar to that of the substrate, indicating the correct epitaxial structure, with the [100] direction of the NiO lattice parallel to the [110] direction of the Fe lattice. The larger spots and reduced contrast of the LEED pattern for the film shows however that the overlayer does not arrange itself as nicely as the substrate does, in analogy with the NiO/Ag(001) case [16]. Further indication on the similarity between NiO/Ag(001) and NiO/Fe(001) films is given from the IPE results, reported in Fig. 1. Here, in panel (a), we present spin resolved IPE spectra for both the Fe(001)-p(1 × 1)O substrate and the NiO/Fe(001) film, taken at normal incidence and room temperature. The spectra are normalized to 100% spin polarization of the incident electron beam and have been collected in magnetic remanence after having magnetized the sample in plane along the [100] easy axis direction of the Fe lattice [20,27]. The substrate lineshapes are dominated by the well known B1 and B2 structures appearing in the majority- and minority-spin channel, respectively [27]. The overlayer spectra show an onset well above the Fermi energy (E_F), reflecting the insulating nature of NiO. Three features at around 3, 6 and 12.5 eV above E_F clearly emerge from the background; a further structure is also present at higher energy (~ 18 eV). Furthermore, it is clear from the spectra that no in-plane spin-polarization dependence is observed whatsoever. This result would be expected for bulk NiO, due to its AFM nature. Here, in fact, the magnetic moments present a FM alignment within each (111) plane, with an AFM alignment of adjacent (111) planes, resulting in a zero overall magnetization. Our data indicate that no in plane net magnetization develops in NiO(001) thin films, even in the presence of an in plane magnetized FM substrate. We note that this result is not trivial if we think of the quite bizarre findings encountered in the field of ultra-

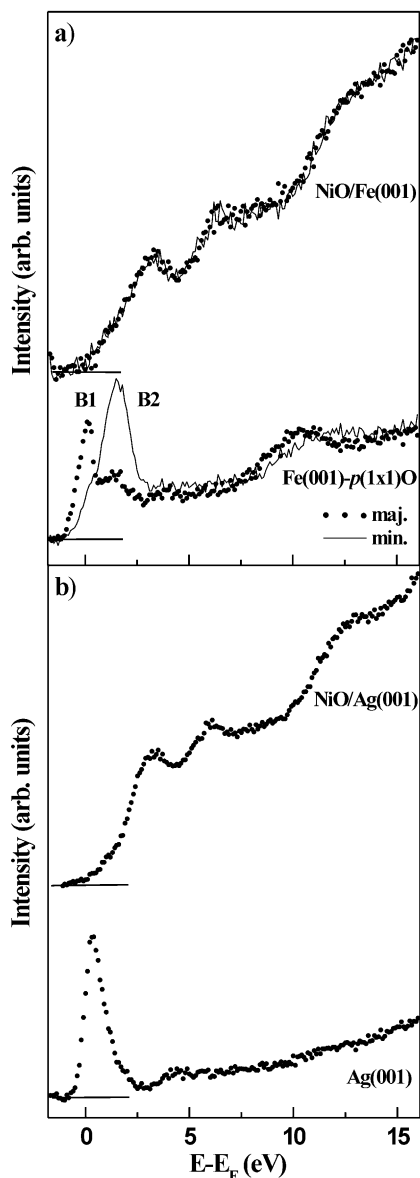


Fig. 1. (a) Spin resolved IPE spectra for the Fe(001)-p(1 × 1)O substrate and the overlying NiO film. In the latter case, no spin dependent character at all can be shown by the various features. (b) IPE spectra for the Ag(001) substrate and the NiO film grown on top of it.

thin film magnetism. Our results are thus consistent with a bulk-like magnetic structure valid for describing thin films as well. However, it should be noted that any alignment of the magnetic moment giving rise to an AFM character would show in

any case an unpolarized result in our measurements. From this point of view also the oxide/metal interface morphology can play an important role influencing the FM/AFM coupling: in similar structures, for example, it has been shown [24] that a 2 ML thick FeO film forms between Fe and NiO.

Direct comparison between NiO/Fe(001) films with those grown in the same conditions onto Ag(001) can be made by inspection of Fig. 1b, where the overlayer and substrate IPE spectra for the latter system are shown. It is seen that the NiO spectrum is basically identical to that of Fig. 1a, with features at the same energies, independently on the very different substrates. A full spectral analysis with attribution of these features to various empty states, involving both Ni 3d and O ligand holes, has been reported elsewhere [16].

On the basis of all these findings we conclude that high quality NiO(001) films can be prepared on Ag and Fe substrates as well. However, having experienced more than a dozen film preparations, a different role of the two substrates has been evidenced. In fact, while for films grown onto Ag we always found IPE spectra as those of Fig. 1b, around one third of the films deposited onto Fe showed slightly different results. In these films, in fact, the IPE spectrum presents a low energy shoulder close to the Fermi level with non-zero signal at E_F , while keeping the usual shape at higher energies. In particular the four NiO features are seen at the same energies, within the experimental accuracy of ~ 0.1 eV. In Fig. 2 IPE spectra for NiO/Ag(001), “good” NiO/Fe(001), and “bad” NiO/Fe(001) films are compared in a restricted energy range close to E_F . For an insulating material, such as NiO, the onset of the IPE signal is expected to occur at energies corresponding to the conduction band minimum (CBM), i.e. well above E_F in undoped intrinsic samples. This is what actually happens in NiO/Ag(001) and most of the NiO/Fe(001) films, the one labeled as good in Fig. 2: in these cases a previous study has shown that the E_F position is nearly centered inside the gap [16]. The occurrence of an IPE signal below the CBM, as seen in the NiO/Fe(001)-related spectrum labeled as bad in Fig. 2, indicates instead

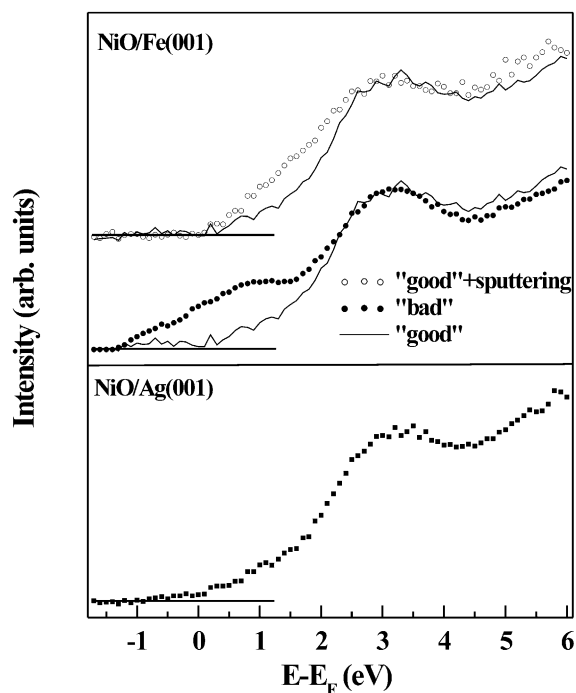


Fig. 2. IPE spectra, close to E_F , for NiO grown both on the Ag(001) (bottom panel) and the Fe(001) (top panel) substrates. For the NiO/Fe(001) system the profile related to the good film is shown together with the lineshape for the bad film and the one for the good + sputtering surface. See text for the meaning of labels.

the presence of states within the gap, which can be attributed to the presence of film defects. The role of defect states in NiO, either bulk or as a thin film, has been recognized long ago and thoroughly discussed (see e.g. Ref. [11]). In order to interpret our data, we use then the following scheme. When growing NiO on Fe substrates, high quality films are obtained in most cases, whereas defect rich films show up in roughly one third of the cases, in a more or less unpredictable manner. Note in fact, that these films were grown in the same conditions as the others: we were not able to put in evidence any difference in the preparation procedure nor correlation with film thickness whatsoever. In order to check this interpretation, we intentionally induced some defects into an otherwise defect-free NiO/Fe(001) film, looking for the effects brought about in the IPE spectrum. This has been done by

subjecting such a film to a mild Ar-ion bombardment. These results also are reported in Fig. 2 where IPE data for a good NiO/Fe(001) film before and after (labeled as good + sputtering) such a treatment are presented. Upon sputtering, the IPE profile keeps basically unchanged above the first peak, while a signal increase is indeed observed closer to E_F . This clearly shows some analogy to the data on what we consider a defect rich film, although the details of the resulting lineshapes are somewhat different since for the bad NiO/Fe(001) sample the defects states go below E_F . Unfortunately is not possible to follow the evolution of the defects states for a stronger sputtering due to the smearing out of the spectroscopic features underneath the background. It has also to be remarked that, as noted above, the energy position of the IPE features is very stable in all the NiO films. This implies that, for the NiO/Fe(001) system, the Fermi level maintains its position roughly at the middle of the gap irrespective of the film quality. This situation is different from what found in bulk NiO where large changes in the position of E_F within the gap were found as a function of the defect density [16,29]. Formation of defects giving rise to both donor-like (e.g. O-vacancies) and acceptor-like (e.g. Ni-vacancies) states with an overall charge neutrality would account for the findings on NiO/Fe(001). Defects are likely to be present also in high quality films, but with much smaller concentration, below the detection limit of our spectroscopic tools. The fact that defect states are sometimes detected in NiO/Fe(001) films and never detected in NiO/Ag(001) films is a clear indication that the former system is more complex than the latter, i.e., stronger overlayer–substrate interactions occur when replacing Ag with Fe. Measurements on thinner NiO films, which would enhance the role of the interface, are made very difficult by the strong substrate emission in the energy range of interest (see Fig. 1).

It is well known that the quality of defect rich samples can be improved by high temperature annealing. When doing that on our NiO/Fe(001) films, we found a dramatic change of the structure, as demonstrated in Fig. 3, reporting XPS

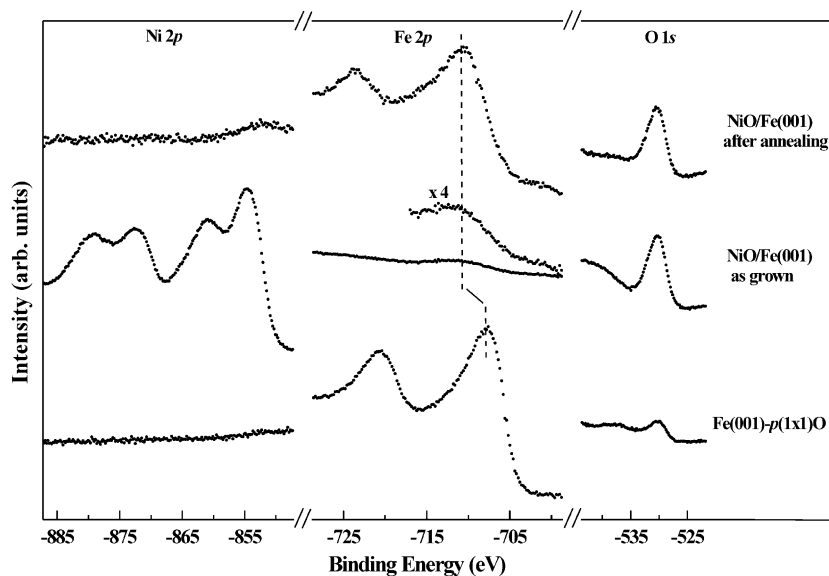


Fig. 3. XPS data related to Ni 2p, Fe 2p, and O 1s core levels, respectively. From bottom up, the spectra refer to: (i) the Fe(001)-p(1 × 1)O substrate, (ii) an as grown 30 Å thick NiO/Fe(001) film, and (iii) the same film after 3 min annealing at 900 K. Intensities have not been rescaled. Note that the small bump, present in case (iii), in the Ni 2p profile at ~852 eV binding energy is due to Fe 2s emission. Concerning the Fe 2p spectra a shift of about 2.8 eV is evidenced comparing the substrate lineshape and the interface.

data in the energy region corresponding to the Ni 2p, Fe 2p, and O 1s core levels. From bottom up, the spectra refer to: (i) the Fe(001)-p(1 × 1)O substrate, (ii) an as grown 30 Å thick NiO/Fe(001) film, and (iii) the same film after 3 min annealing at 900 K. For each of the involved core levels we have the following evolution: (1) the O 1s signal intensity increases, starting from the value corresponding to 1 ML (in the substrate), to a much larger value in the oxide film, with no significant effect upon annealing; (2) the Fe 2p signal intensity is strongly reduced upon NiO formation, as expected, but then it undergoes a remarkable increase upon annealing; (3) the Ni 2p signal is obviously absent on the substrate and appears in the film with the typical NiO-like lineshape, namely with a satellite feature accompanying each main spin-orbit split peak; it then disappears again upon annealing. Note that the small bump present after the annealing (and barely visible in the substrate lineshape as well) is due to the Fe 2s emission. These results indicate that, in agreement with

thermodynamic considerations, a Ni–Fe atoms substitution occurs in the film, leading to the formation of an Fe-oxide top layer, while Ni atoms diffuse and dissolve into the bulk. A closer look to the XPS spectra of Fig. 3 supports this interpretation. In fact, it is seen that the Fe 2p profile in the annealed sample has a lineshape typical of oxides, i.e. wider than the pure metal lineshape due to a large asymmetry in the low kinetic energy side [30], with a chemical shift of ~2.8 eV with respect to metal Fe. The O 1s lineshape keeps unchanged while Fe substitutes Ni in the oxide.

On the basis of the similarity between the FeO and NiO lattice, we propose that the metal atom exchange mechanism leads to formation of iron monoxide. The misfit between the Fe substrate and FeO is small enough (6%) to be consistent with epitaxy. Note also that after annealing the LEED pattern remains practically unchanged, with only a slight contrast improvement and background reduction. The measured value of the Fe 2p chemical

shift upon oxide formation is also consistent with that of FeO [30,31], while a much larger value (of ~ 4 eV) would be expected for both Fe_2O_3 and Fe_3O_4 [30–32].¹ Finally, we note that the profile of the Fe signal coming from the as grown NiO/Fe(001) film is very similar to that of the annealed interface both in terms of lineshape and binding energy, indicating that an iron oxide layer is formed also at the interface during the NiO growth, due to interface intermixing. Its thickness is estimated to be around 2 ML in analogy with the results of Ref. [24], despite the different termination of the substrate before NiO growth. By studying the annealing temperature dependence of this system, we have found that such Ni–Fe atom exchange becomes important above 600 K: at such a temperature 5 min are enough to completely convert into FeO a 30 Å thick NiO film.

As a final point, concerning the formation of an Fe oxide upon thermal treatment of the NiO/Fe(001) interface, we show in Fig. 4 the IPE spectrum for the resulting FeO/Fe(001) film: it shows just one peak at about 2 eV above E_F and is considerably different from the NiO profile. In the same figure the IPE spectrum taken from a polycrystalline FeO sample, as reported in Ref. [33], is also shown for a comparison. The overall similarity between the two spectra seems again to suggest that the film formed upon annealing has the monoxide stoichiometry. However, we note that the relevance of this comparison should not be pushed too far since (i) the experimental conditions are different (normal incidence on single

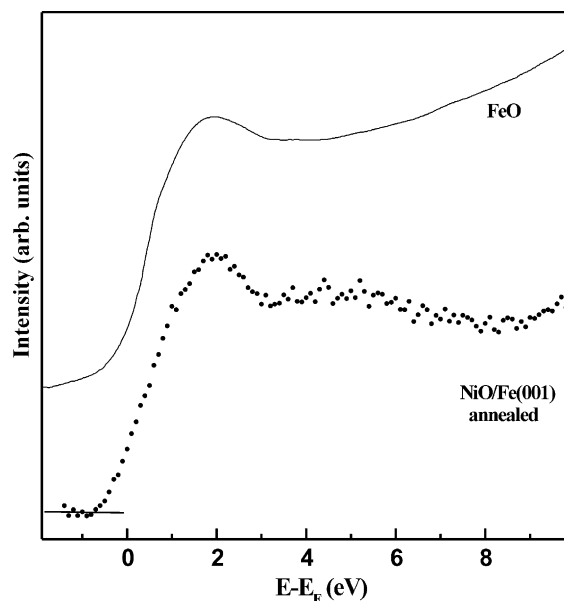


Fig. 4. IPE results for the NiO/Fe(001) surface after annealing compared to reported IPE data ($h\nu = 18$ eV) on stoichiometric FeO [33].

crystal (001) faces vs angle integrated on polycrystal) and (ii) the IPE profiles of the other Fe-oxides, namely Fe_2O_3 and Fe_3O_4 [34], do not differ very much from the profiles of Fig. 4.

4. Conclusions

We have shown that single crystal NiO film can be effectively grown on top of a FM substrate, opening a new field to investigations of the AFM–FM interface phenomena. XPS, IPE and LEED observations demonstrate that these epitaxial NiO/Fe(001) films may be as good as those grown on Ag(001). Photoemission and IPE results indicate that NiO/Fe(001) films have an electronic structure similar to the bulk and in turn to NiO/Ag(001) films. Moreover, at variance with the FM substrate, no polarization effects are observed in spin resolved IPE, in agreement with the AFM nature of NiO. Our data shows that this holds true also for thin films, even in the presence of a FM substrate. Ni–Fe interaction makes however the overlayer–substrate interface more complex than

¹ In principle some surface core level shifts can occur in these spectra due to the reduced dimensionality, which might influence the above arguments. In fact these shifts are generally smaller than those quoted here between FeO and the higher oxides. Furthermore, according to the estimated electron escape depths (λ) for metal oxides (see [32]) expected λ for the Fe 2p kinetic energy, as excited by MgK α photons, is ~ 20 Å; this value is compatible with the fact that, in Fig. 3, the Fe 2p signal is still visible beneath the 30 Å thick NiO film even before annealing. Therefore the signal comes out from a number of layer large enough to mask the surface effects (generally confined within the two topmost layers for well ordered structures). For example, the Fe 2p profile of the Fe(001)-p(1 \times 1)-O surface is not distinguishable from the pure Fe(001) lineshape.

in NiO/Ag(001) films. This can lead in some case to defect formation within the NiO film, which shows up in the IPE spectra in terms of states inside the NiO gap. Annealing gives rise to a Ni–Fe atom exchange in the thin oxide film, resulting in the formation of an Fe-oxide top layer, whose stoichiometry we suggest being FeO. As a by-product the present study yields a new method for preparing high quality thin FeO(001) films, which constitutes an important result per se and surely deserves further investigations.

Acknowledgements

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